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The Separation of Plutonium from Platinum by Coprecipitation with Ferric Iron Followed by Ion Exchange on Inorganic Exchange Materials

by

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THE SEPARATION OF PLUTONIUM FROM PLATINUM BY COPRECIPITATION WITH FERRIC IRON FOLLOWED BY ION EXCHANGE ON INORGANIC EXCHANGE MATERIALS

G. L. Johnson and E. B. Fowler

ABSTRACT

A method is described for the separation of trace amounts of plutonium from macro amounts of platinum.

Platinum solutions, prepared from the metal contaminated with plutonium, are subjected to several scavengings with ferric ion. The resulting precipitates of hydrous ferric oxides are filtered and the final filtrate treated with hydrogen peroxide and nitric acid to reduce the plutonium to a form which will be retained by the ion exchange medium. Subsequent treatment by passage through a column of either ammonium molybdophosphate or zirconium phosphate serves to remove any residual plutonium remaining after coprecipitation with ferric ion.

The method is rapid and efficient, giving high decontamination factors under the conditions studied.

INTRODUCTION

Nuclear research involves the problem of contaminated materials. Such materials, frequently contaminated with long-lived radioisotopes, are often economically of sufficient value to be worth the effort of recovery. One of the most common materials so encountered is platinum ware.

As part of a platinum-recovery project it became necessary in this Laboratory to derive a method for separating trace amounts of plutonium from macro amounts of platinum. A procedure for accomplishing this separation has been devised that is both rapid and efficient. Advantage has been taken of the fact that, even at trace concentrations where the amount of plutonium is too small to exceed the solubility product of highly insoluble compounds, plutonium is quantitatively coprecipitated from solution with ferric ion. It is a recognized fact that when a solution of ferric ions is treated with a slight excess of OH^- the precipitate of hydrous ferric oxides formed has an enormous surface area.[1] This leads to adsorptive removal of trace amounts of plutonium from solution by coprecipitation with ferric iron. Generally, the plutonium will coprecipitate if the bulk anion forms an insoluble plutonium salt with plutonium in a particular oxidation state.[2,28] Use is also made of the known high selectivity of certain inorganic ion-exchange materials for plutonium.

Rather extensive studies have been made on the exchange properties of both ammonium molybdophosphate (AMP) and zirconium phosphate (ZP), the two exchangers used in this study.[3-19] Most of these studies were

concerned with elements other than members of the transuranium series, although with the awakening of interest in these and other inorganic exchange materials, some early investigations on the exchange of uranyl ion on ZP were made.[20] A more recent investigation of the separation of alpha emitters on ZP is to be found in the literature.[21] In this Laboratory both AMP and ZP have frequently been employed to separate trace quantities of uranium, americium, and plutonium from solutions containing their salts.[22]

EXPERIMENTAL

Reagents and Apparatus

Solutions:

Ferric Iron Solution. This solution was prepared by dissolving 24.2 g $FeCl_3.6H_2O$ in 1 M HNO_3 and diluting to 500 ml with 1 M acid. The solution contained 10 mg Fe^{+3} per ml.

Standard Sodium Hydroxide Solutions. 0.1, 1.0, 6, and 16 M.

Standard Nitric Acid Solutions. 0.01, 0.1, 1.0, and 8 M.

Hydrochloric Acid Solution. 1:9 Dilution of concentrated HCl.

HNO_3-HCl Solution. 1:3 Concentrated acids.

Ammonium Nitrate Solutions. 0.01 and 0.1 M.

Macerated Filter Paper.

All reagents were prepared from analytical grade chemicals.

Ion-Exchange Materials:

Ammonium Molybdophosphate. Bio-Rad AMP-1 (microcrystals) Bio-Rad Laboratories, Batch # 1250-T. South 32nd, Richmond, California 94804.

Zirconium Phosphate. Bio-Rad ZP-1, 100-200 mesh.

Asbestos. Acid washed (Bio-Rad Labs.).

Beckman Model DU Spectrophotometer.

RLD-1 Frisch Grid Chamber. (Tracerlab, Inc.), p-10 gas flow.

RIDL Model 34-12 Transistorized 400-Channel Pulse Height Analyzer. (Radiation Instr. Development Lab., Inc.).

LASL Pulse Amplifier (Model No. PA-6) Decade Scaler (Model No. SC-8B) Alpha Counter. Methane flow, 3-in. counting chamber with 2π geometry.

Stainless Steel Counting Plates. Approximately 2 in. ø x 0.01 in. thick.

Ion-Exchange Columns. The columns consisted of a 12-cm length of glass tubing, 18 mm ID, sealed to a 9-cm length of tubing, 6 mm ID, and fitted with a drip tip.[24] Three equally spaced indentations were made approximately 0.5 cm from the tip to retain the plug of glass wool used to support the exchange material in the column.

Preparation of Ion-Exchange Columns

An exchanger bed of ZP was prepared by adding a slurry of the exchange material in 0.1 M HNO_3 to a column containing a glass wool plug. The column was washed with 0.01 M HNO_3 until the effluent was clear.

AMP columns were prepared by first mixing the exchanger with acid washed asbestos in the ratio 1:2, w/w.[18] A slurry in 0.1 M NH_4NO_3 was then prepared from this mixture and the column prepared as for ZP.

Preparation of the Sample

Platinum metal contaminated with plutonium (6×10^5 c/m alpha activity) was dissolved in the 1:3 HNO_3-HCl solution. It was necessary to heat this mixture gently to bring about complete dissolution of the platinum metal. The resulting solution was then diluted to a known volume with distilled water. An aliquot of this stock solution was diluted ten-fold with distilled water before carrying out the separation.

Coprecipitation of the Plutonium with Ferric Iron

To 50 ml of sample was added 1 ml of ferric iron solution. The sample was heated to near boiling. The iron was precipitated by the addition of the appropriate standard sodium hydroxide solution. The

base was added dropwise with rapid stirring until a pH of 4-6 was obtained. A small amount of macerated filter paper was added to the beaker containing the gelatinous precipitate to facilitate filtration. The solution was then filtered, while hot, on Whatman No. 41H filter paper. The precipitate on the paper was washed with a small amount of hot water and the washings and filtrate was scavenged twice more with ferric iron. The final filtrate was saved for column treatment.

Removal of Residual Pu by Ion Exchange

The combined filtrates were acidified with 1-2 ml concentrated HNO_3, and 1 ml of 30% H_2O_2 was added. The beaker was covered with a ribbed watch glass, placed on a steam bath, and the solution taken to incipient dryness over a period of time sufficient to reduce* all the plutonium.[25] The residue was dissolved in approximately 10 ml 0.1 M HNO_3 and the resulting solution passed through a prepared column of either AMP or ZP. The column was washed with sufficient 0.1 M NH_4NO_3 (AMP) or 0.1 M HNO_3 (ZP) to give a colorless effluent. Effluent fractions were collected and analyzed for alpha activity and platinum.

Determination of Platinum

Platinum was determined colorimetrically as the iodide at 510 mμ.[23]

RESULTS AND DISCUSSION

The concentration of platinum in the solution resulting from dissolution of contaminated platinum metal was 118 mg/ml. The alpha activity was 7×10^4 c/m/ml.

It was desired to have a solution sufficiently dilute that not only would the platinum remain in soluble form during acid digestion of the sample and its subsequent evaporation with H_2O_2, but also that the self-absorption of the alpha activity due to the residue remaining on the counting plate after drying and flaming would be reduced to a minimum. For this reason platinum determinations were made on 1:10, 1:100, 1:500, and 1:1000 dilutions of the platinum stock solution in order to determine the optimum platinum concentration. It was found that there was little advantage in using a dilution greater than 1:10 unless one were willing to accept a decrease in counting precision.

Table 1 shows data obtained from typical runs using a 1:10 solution of the stock platinum solution.

*If the HNO_3-H_2O_2 treatment produces Pu (III) it does not seem likely under the conditions of the experiment that the plutonium remained as such.[26]

TABLE 1. REMOVAL OF TRACE PLUTONIUM FROM A PLATINUM SOLUTION (0.590 g platinum/50 ml solution)

	Alpha Activity Observed, c/m/ml					
	AMP Column			ZP Column		
Description of Sample	Exp 1	Exp 2	Exp 3	Exp 1	Exp 2	Exp 3
Stock platinum solution (1:10 dil)	7000	7000	7000	7000	7000	7000
Final filtrate after iron scavenges	27	136	87	71	27	83
Combined column effluents and wash effluents	<1	0	<1	<1	0	0

Table 2 gives the results of a similar run made on the solution spiked with ^{239}Pu. In each instance the residual activity remaining in the final column effluents was most likely due to the presence of a small amount of uranium and/or americium. This was shown by pulse-height analyses of effluent samples. That this is reasonable is seen from the fact that, either uranyl ion or americium ion alone or both together are far more easily removed from either a column of AMP or ZP than is the adsorbed plutonium. Choice of elutriant concentration is not critical for desorption of either species. With nitric acid (or HNO_3 + NH_4NO_3) concentration up to 3 M both species are effectively removed from the exchanger while the plutonium remains firmly fixed.

TABLE 2. REMOVAL OF TRACE PLUTONIUM FROM A SPIKED PLATINUM SOLUTION
(0.590 g platinum/50 ml solution)

Description of Sample	α Activity Observed c/m/ml	Decontamination Factor
Spiked sample	7×10^5	
Final filtrate after iron scavenges	14	5×10^4
Combined column effluents and wash effluents:		
AMP column	2	3.5×10^5
ZP column	4	1.8×10^5

Figures 1 and 2 show the elution curves for the separations under study. Platinum is not adsorbed on the column since dissolution of platinum metal in aqua regia leads to the formation of $\left[PtCl_6\right]^=$;[27] hence, there can be no true exchange with a cationic exchange material. The $\left[PtCl_6\right]^=$ is as readily washed from either column with distilled water as with dilute acid or salt solutions.

The total platinum concentration was generally maintained throughout the procedure. Virtually all of the platinum was carried through the coprecipitation step.

The maximum loss encountered during this investigation was 0.010 g/50 ml solution. No loss of platinum occurred during column treatment. On the average a recovery of 99.4 ± 0.5% was realized.

The sharp uranium and/or americium band noted in Fig. 2 does not appear among the curves for AMP (Fig. 1). This is due to the lower selectivity of AMP for plutonium than is exhibited by ZP. Being more weakly absorbed on AMP some 85% of the plutonium is eluted from the column, along with the other weakly adsorbed activities, by the first two column volumes of elutriant. On the other hand, plutonium in our solutions was more strongly adsorbed on ZP than was UO_2^{++} or Am (III); thus the first column volume of elutriant effectively removes UO_2 and/or Am (III) in a sharp band before plutonium began to elute. The plutonium was eluted from the column only with difficulty.

The removal of the plutonium from solution with ferric iron before column treatment is not obligatory. It merely serves to reduce rapidly and efficiently the amount of alpha activity added to the column and, hence, to increase the useful life of the column.

Results comparable to those given were obtained using column treatment alone. The decontamination factors, however, were generally slightly lower. In any case, 98% or more of the platinum was carried through the procedure.

CONCLUSION

The separation of trace amounts of plutonium and other alpha emitters from macro amounts of platinum has been practically accomplished by the procedure described. The method outlines a unique and rapid means of carrying out this separation. Since most of the alpha emitters likely to be encountered in routine work are at least weakly adsorbed on either AMP or ZP, the method not only allows their separation from

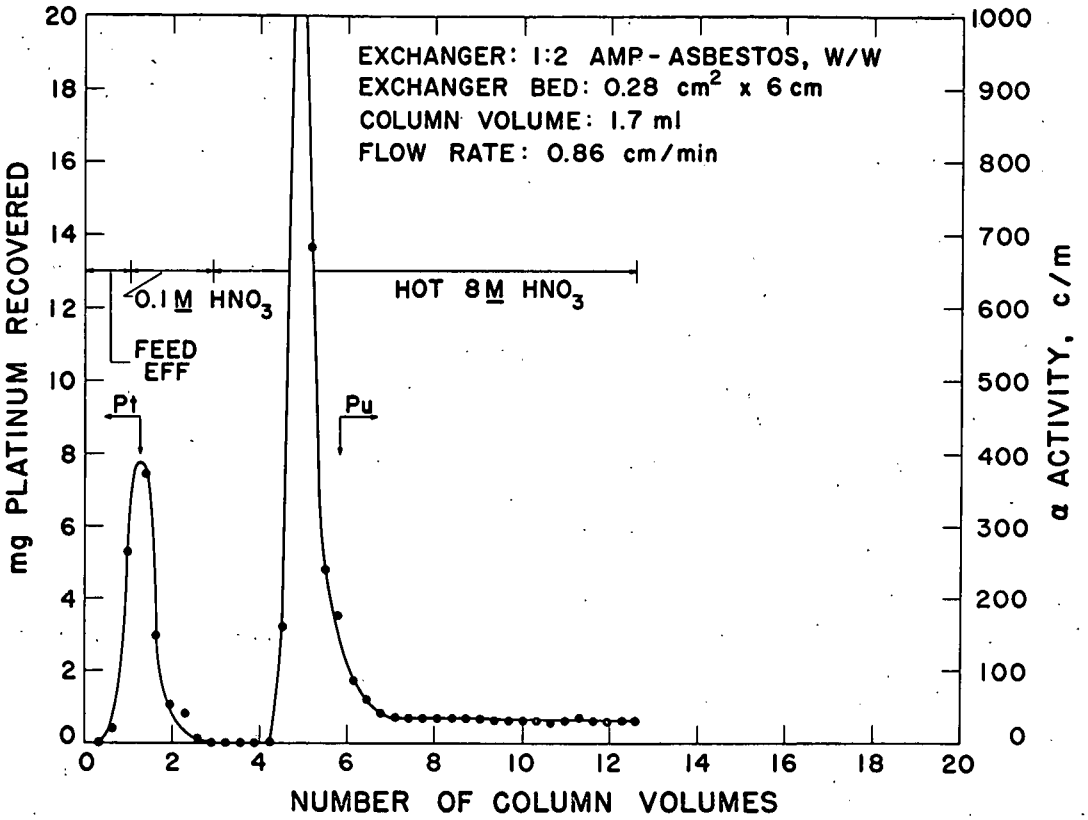

Fig. 1. Separation of Platinum and Contaminating Alpha Activity on an AMP Column.

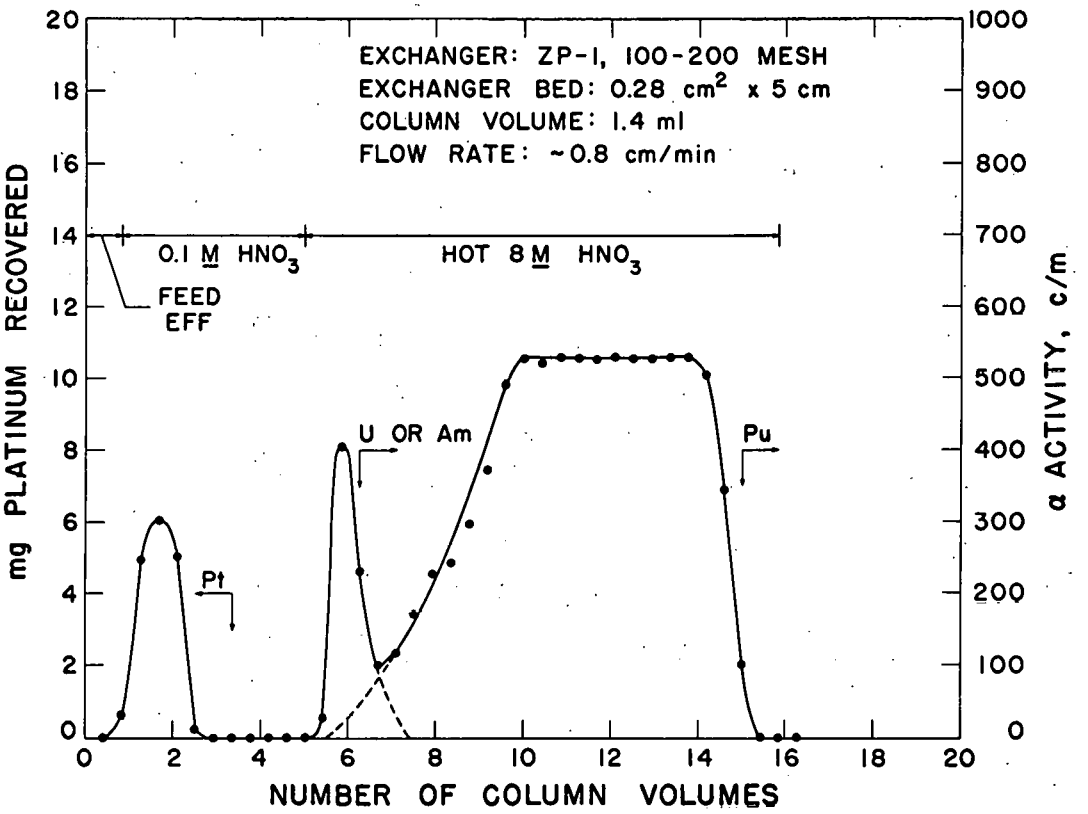

Fig. 2. Separation of Platinum and Contaminating Alpha Activity on an ZP Column.

platinum but also their identification if present in sufficient amounts.

This method may provide for the decontamination of platinum metal and its subsequent reclamation as metallic platinum or as platinum sponge. Sponge produced from the recovery of platinum has been used as a filter for the removal of radioactivity from gas streams.

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